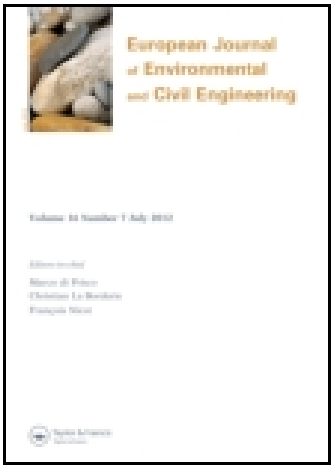

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An extensive study in blended cement pastes that comprised two different experimental settings was carried out so as to analyse the hydration process and compressive strength evolution up to 91 days. The aim of this study was to understand the hydration process using zeolite-rich tuffs and siltstone as supplementary cementitious materials at low water-to-binder ratio (W/B = .3) under wet curing condition. It was observed that there were two competing reactions, i.e. pozzolanic reaction and carbonation, during the hydration process, thus leading to a decrease in the content of calcium hydroxide (CH); however, carbonation played a more important role than the pozzolanic reaction in consuming it at the given W/B ratio. The total amount of CH consumed by pozzolanic reaction was likely around 8%, while carbonation transformed around 19% of the total amount of CH at 91 days. Although fully hydrated cement paste incorporates .23 g of water per g of cement, only 60% of this value was used at such a W/B ratio. In addition, the amount of normalised water in hydrates increased as the dosage increased by factor of .158% per 1% of dosage. Finally, the optimal dosages at which Zeo1, Zeo2 and Limo showed the highest compressive strength were in the ranges of 12.5–15%, 17.5–20% and 10–12.5%, respectively .

Keywords: pozzolanic reaction; natural zeolite; hydration process; quantitative X-ray diffraction; blended cement

1. Introduction

Natural zeolites are widely available all over the world, and hence a number of applications in cement-based materials have been reported (Ahmadi & Shekarchi, 2010; De Gennaro & Langella, 2008; Feng & Peng, 2005; Karakurt & Topçu, 2012; Valipour, Farhad, Shekarchi, & Khani, 2013). Generally speaking, most of the zeolitic tuffs used as supplementary cementitious materials (SCMs) are mainly composed of Mordenite (MOR), Heulandite–Clinoptilolite (HEU–CLI) cojointly with quartz (Qz), clays and other minor phases (Hay & Sheppard, 2001). However, this mixture presents a wide range of performances because not only the mineralogical composition, but also the chemical one as well as water-to-binder (W/B) ratio and curing condition exert significant effects on engineering properties (Lothenbach & Scrivener, 2011; Schneider & Romer, 2011; Thomas, Hooton, Scott, & Zibara, 2012).

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The use of zeolitic tuffs as SCMs depends mainly on the microstructure and chemical composition. In case of microstructure, Fragoulis et al. highlighted that MOR-rich tuffs are denser than CLI–HEU ones, despite MOR and HEU having almost similar chemical composition. The authors also reported that MOR blends showed better compressive strength than HEU ones under similar experimental conditions (Fragoulis, Chaniotakis, & Stamatakis, 1997). In case of chemical composition, it has been reported that more siliceous zeolite reacted faster and developed better mechanical properties; in contrast, less siliceous zeolites did not, but instead consumed more calcium hydroxide (CH) than silica-rich counterparts (Mertens et al., 2009; Perraki & Kontori, 2010). If such were the case, the difference in mechanical performance could be due to the content of reactive silica. In this sense, a general consensus is that reactive silica can be readily combined with CH then producing calcium silicate hydrate (CSH) (Antiohos & Tsimas, 2005; Davraz & Gunduz, 2005; Papadakis, 1999; Talero & Trusilewicz, 2011) and zeolites contain a significant amount of reactive silica; in fact, the early mechanical evolution could be directly related to the amount of reactive silica (Blanco Varela, Martinez Ramirez, Erena, & Gener, 2006; Martinez Ramirez & Blanco Varela, 2006; Uzal, Turanlı, Yücel, & Göncüoğlu, 2010; Yılmaz & Uçar, 2007).

The pozzolanic reaction between zeolites and CH during the hydration process leads to consumption of CH and extra production of CSH. Caputo et al. pointed out in detail how important the crystalline state of zeolites is during the pozzolanic reaction and the principal steps followed by zeolites during the pozzolanic reaction as follows: (1) cation exchange; (2) dissolution or breakdown of zeolites structure; (3) possible formation of transient gel phases; and (4) precipitation of CSH and calcium aluminosilicate hydrate (Caputo, Liguori, & Colella, 2007).

Many authors highlighted that cation exchange of zeolites is extremely important during hydration at early age. Luke identified that cation exchange could take up Ca^{2+} at early ages, even it was the major responsible of its depletion; but latter, pozzolanic reaction could consume more Ca^{2+} than cation exchange alone (Luke, 2007). In addition, the released alkali cations accelerated the hydration process (Snellings, Mertens, Cizer, & Elsen, 2010; Snellings, Mertens, Hertsens, & Elsen, 2009; Yılmaz & Uçar, 2007). Mertens et al. additionally reported that cation content and external surface in zeolites play an important role at early ages, but also at long term (Mertens et al., 2009).

The optimal amount of mineral addition used as SCM plays a crucial role in the economical and environmental evaluations of composite cements. A number of studies of natural zeolite used as cement replacement has been reported in order to optimise its usage (Ahmadi & Shekarchi, 2010; Ganesan & Rajagopal, 2007; Pekmezci & Akyüz, 2004; Valipour et al., 2013). Perraki et al. pointed out that 10% of HEU-rich tuff showed better mechanical properties than control samples; but at higher amounts, CH could not be consumed completely (Perraki, Kakali, & Kontoleon, 2003). Tükmenoglu and Tankut widened the optimal values proposing the range of 10–20% of dosage because of impurities and other stable phases like Qz. In this sense, the author also reported that clay and other impurities had an adverse effect on the mechanical properties (Türkmenoğlu & Tankut, 2002).

Comparing natural zeolites to other pozzolanas, Poon et al. stated that CLI, in terms of pozzolanic reactivity, is in between fly ash and silica fume (Poon, Lam, & Kou, 1999). Luke, on the other hand, stated that MOR shows a higher degree of hydration when compared with Chabasite, although he also reported that MOR retarded the hydration while Chabasite accelerated it (Luke, 2007). Scrivener et al. recently reported

that zeolites react faster than fly ash and slag despite the fact that zeolites are more crystalline than the other two (Scrivener & Nonat, 2011).

Although the pozzolanic reaction proceeds during hydration at high W/B, it diminishes as W/B ratio decreases. Meeks summarised the effect of curing on high-performance concrete highlighting that at lower W/B, blended cement requires longer periods of curing in order to avoid some detrimental effects like self-desiccation, strength depletion, and volume changes, as well as finally pointing out that the critical W/B is .42 (Reference in Meeks & Carino, 1999).

It is noteworthy that a lot of work has been done regarding natural zeolites used as SCMs; however, there is still a gap in scientific literature with regard to hydration process using natural zeolites at low W/B ratio (W/B = .3) and cured under water without any chemical addition which should induce some adverse effect on the final performance. This study includes a comparison of zeolites and other pozzolana like calcareous siltstone in order to propose an optimal dosage to be used.

2. Experimental procedure

2.1. Materials

Cement pastes were blended in order to evaluate the effect of SCMs on compressive strength and hydration products by varying the proportions and curing days. SCMs were two zeolite-rich tuffs coded as Zeo1 and Zeo2, and one siltstone coded as Limo that were blended with ordinary Portland cement (OPC).

Table 1 provides mineralogical and chemical composition of both zeolite-rich tuffs according to UNE EN 196-2:1996; UNE 80217:1991; UNE 80225:1993 EX; UNE EN 451-1:1995. This table indicates that Zeo2 is composed of a mixture of MOR and

Table 1. Chemical and mineralogical compositions of zeolitic tuffs and siltstone.

Chemical composition (%)	Zeo1	Zeo2	Limo
Si_2O total	68.24	65.99	55.09
CaO total	3.71	4.75	19.67
Al_2O_3	11.46	10.98	4.27
Fe_2O_3	4.08	3.90	2.18
MgO	.96	1.48	.78
IR	13.03	6.31	9.09
SiO_2 reactive	57.27	60.97	47.77
CaO reactive	3.34	3.33	4.95
SiO_2/(MgO + CaO)	15.87	13.72	9.61
Mineralogical composition (%)			
HEU–CLI		23.30	8.00
MOR	73.1	45.5	
Qz	17.4	11.4	47.00
Cc		14.00	27.00
Anorthite	.8		
Montmorrillonite			15.00
Cristobalite			3.00
Amorphous	8.7	5.9	~1
Density[a]	2.29	2.18	

[a]ASTM C188 Density of hydraulic cement.

HEU–CLI, and Zeo1 contains much more MOR than Zeo2. These results are in agreement with those of others reported previously, where it has been additionally informed that these zeolites are Ca-clinoptilolite, Ca-heulandite and Na-Ca-MOR because of high Ca values in cation exchange tests (Machiels, Snellings, Morante, & Elsen, 2006; Machiels et al., 2008, 2014). On the other hand, Limo is a calcareous siltstone, which is currently being used as mineral addition in pozzolanic cement because of its closeness to cement plant.

The physical and chemical characteristics of OPC used in this study are summarised in Table 2. This information was provided by the technical staff of the cement plant. It can also be observed in this table that some reference data have been provided by Ecuadorian standard NTE-INEN 152. All physical and chemical characteristics of the cement were according to the Ecuadorian standards.

2.1.1. The pozzolanic activity: the Frattini's test

The Frattini's test was done to evaluate the pozzolanic activity of these samples, as can be seen in Table 3. This table provides useful information about the consumption of Ca^{2+} by the SCMs at the ages of 7 and 15 days compared to the lime solubility curve. The procedure used in this study can be found in EN-196-5.

2.2. Sample preparation

SCMs were collected from outcrops close to Guayaquil and the organic matter was immediately separated. After that, all samples were ground using a hammer for a while, then crushed by a jaw mill at different time; finally, a ball mill was used, thus reducing the grain size to almost 70% by weight passing sieve N 375 mesh. This methodology was followed for all samples, but by changing the milling time because these samples possessed different hardness levels.

Table 2. Physical and chemical properties of OPC.

Characteristics	INEN 152[b]	OPC[a]
Chemical		
LOI % max	3.0	.8
MgO	6.0	1.0
SO_3	3.5	2.8
IR% max	.75	.4
Physical		
Length change for autoclave, % max	.8	.012
Setting time initial no less than, min	45	149
Final no more than, min	375	259
Air content, % max	12	3.5
Compressive strength (MPa)		
1 day		15.2
3 days	12	26.9
7 days	19	36.4
28 days	28	46.1
Equivalent alkalis % max	.6	.4
False setting. Penetration % min	50	75.0

[a]As reported by the Cement Plant Quality department.
[b]Ecuadorian cement standard.

Table 3. Frattini test results for Zeo1, Zeo2 and Limo at 7 and 15 days.

		OH^-		CaO		Theoretical (CaO)		Results
Sample	Age (days)	Volume HCl (ml)	Concentration (mmol/L)	Volume EDTA (ml)	Concentration (mmol/L)	max [CaO] (mmol/L)	reduction in %	
Zeo1	7	21.10	42.4	26.19	15.6	27.4	43	No
	15	18.6	37.4	16.84	10.1	22.4	54.9	Ok
Zeo2	7	18.4	37.0	17.47	10.4	22.0	52.7	Ok
	15	19.5	39.2	14.04	8.4	24.2	65.3	Ok
Limo	7	22.5	45.2	25.56	15.3	30.2	49.3	No
	15	20.10	40.4	20.43	12.2	25.4	51.9	Ok

2.3. Experimental settings: calibration and replication

In this study, two different experimental settings were used, i.e. calibration and replication. The aim of using two slightly different experimental settings was to analyse small variations in proportioning and testing time, but simultaneously these results could compare each other so as to verify the results over the whole experimental range. Phenomenologically speaking, the variation due to mineral addition can be estimated without repeating the same combination of factors and levels, thus allowing the analysing of more data under same experimental conditions. A randomised block with one blocking factor was used as experimental design for both experimental settings. The experimental factor was the proportioning including OPC as control (0% of mineral addition). Since it was designed as an equidistant experimental design, each level of proportion was chosen by adding 5% of SCM. In case of calibration, this means 5, 10, 15, 20 and 25% including 0% (as control). The curing/testing days were selected as blocking factors so as to decrease the variability. In this sense, this experiment was carried out up to the age of 91 days because the pozzolanic reaction is a long-term reaction. Like proportioning, the age of testing was also carried out equidistant every 7 days i.e. 7, 14, 21, 28 and 91 days.

In case of replication, this experiment was replicated with a slight change in terms of proportioning and testing days. The proportioning was selected as follows 7.5, 12.5, 17.5, 22.5 and 27.5%, while the testing days were 4, 11, 18, 25 and 91 days. The selected W/B was .3. This ratio remained constant during the experiment.

In addition, ASTM C109 was selected as standard to test the mechanical performance. In this case, 50-mm cube moulds were used according to this standard. Once samples were mixed using tag water at W/B ratio of .3, a vibrating table was used to assure that no bubble was present inside the specimens according to ASTM C230. Next, a mixture of 750 g was poured into 3-cube moulds, thus allowing the calculating of the standard errors and means. The specimens were then moulded inside 3-cube moulds as soon as possible to avoid the loss of material and undesired setting. After that, paraffin films were placed over the open side of cube to avoid the evaporation. Before demoulding, the specimens were set and hardened into cube moulds for 24 h, finally each specimen was driven to the curing site. In this experiment, wet curing condition means that specimens were soaked under water at room temperature up to testing day. In addition, it is noteworthy that lime-saturated water was not used in order to do a more realistic experiment; hence, carbonation would play a meaningful role during the hydration process, and it must be taken into account for calculation.

2.4. Compressive strength

ASTM C109 was used as standard for testing specimens at the specified day after curing period. A Shimadzu® universal testing machine (600 KN) with an accuracy of .5% was used for compressive strength tests. Once the universal testing machine broke the hardened cement cubes, some small broken pieces were chosen to be stored under ethanol in a hermetically closed bottle of 100 ml so as to stop the hydration prior to other tests. It is possible that ethanol could react with hydration products as reported by Knapen, Cizer, and Van Balen (2009), but its effect on microstructure is cannot be completely accepted (Makar & Sato, 2012).

2.5. Analytical techniques

2.5.1. Quantitative X-ray diffraction

PANanalytical® X'pert XRD with $K\alpha$ Cu anode tube was used. X'Celerator®, a multi-position detector, was used to collect the data as fast as 3 min. The operating conditions were: 40 mA and 45 kV, step size of .02, and Cu $K\alpha 1$ radiation. In addition, High Score Plus® software was used to identify and to quantify the crystalline phases conjointly with amorphous content.

For the quantification of hydrated phases in cement pastes and raw materials, Rietveld refinement methodology was used to compare the observed diffractograms and the theoretically calculated ones from the structural database by the means of least-squared method up till the best fit is reached (Mitchell & Margeson, 2006; Whitfield & Mitchell, 2003). In order to identify the crystalline phases, the patterns shown in Table 4 were used in the theoretical structures for either hydration products or raw materials. It is important to notice that corundum was used as internal standard.

The experimental procedure was as follows: samples which remained inside the hermetically closed bottle under ethanol were collected at the planned age. The selected pieces were afterwards put inside a desiccator during next 5 days in order for the samples to dry. The dried samples were then ground by using a pestle and mortar as soon as possible to avoid further carbonation. Finally, this powder was sieved though sieve N 325 mesh, the passed powder was mixed with 10% by weight of corundum as internal standard and 1 g of mixture was placed on an XRD sample holder for measurement.

2.5.2. Thermal analysis

The weight losses and heat flows, as functions of temperature, were measured using a simultaneous TA® thermal analyser (TGA-DSC) and evaluated by Universal analysis ®software. After drying in a desiccator for 5 days, the milling process was carried out by using mortar and pestle. It is noteworthy that this treatment was done on all the samples. Next, 10 grams of aliquot from the milling process was poured into 90 µl alumina crucibles and heated from room temperature up to 1100 °C at the rate of 20 °C min^{-1} and 100 ml/min as nitrogen flowing rate. The results of thermogravimetric analysis (TGA) were used to quantify the amount of CH, normalised water in hydrates and calcite (Cc), and these are showed in Figures 3–5. The equations used for calculating

Table 4. Reference code of ICDD database of the most abundant identified phases.

	Reference code ICDD			
Phases	Zeo1	Zeo2	Limo	Cement
Mor	00-055-0163	00-055-0163		
HEU–CLI		00-039-1383		
Qz	01-070-7344	01-074-3485	01-085-0798	
Cc		01-083-0578	01-072-4582	01-072-4582
Anorthite	00-041-1481			
C3S				01-072-4582
C2S				01-083-0464
CH				01-081-2041
AFm				01-083-1289
AFt				00-041-1451
Scawtite				01-070-1279

these parameters can be found elsewhere (Borges, Costa, Milestone, & Lynsdale, 2010; Cornejo, Elsen, Paredes, & Baykara, 2014; Kontori, Perraki, Tsivilis, & Kakali, 2009).

The consumption of CH occurred due to the pozzolanic reaction. In order to evaluate the pozzolanic reaction, two main effects were taken into account, such as dilution and carbonation. These two effects played important roles in decreasing the CH content during the hydration (Behim, Cyr, & Clastres, 2011). In this case, for isolating the dilution, the parameters should be expressed over cement content. The total amount of CH consumed by the pozzolanic reaction, which is the result of mass balance between the total amount of CH produced in both plain and blended cement pastes, was calculated by using Equation (1). The parameters in Equation (1) were calculated as follows. In case of the content of CH in both control and blended cement pastes, CH^t was estimated as the amount of CH measured by TGA and then normalised to cement content. In case of the content of carbonated CH, the CO_2 content calculated by TGA was stoichiometrically transformed to CH, and in cases when the mineral additions beforehand contained Cc (see Table 1) this was corrected from the calculation and finally normalised to cement content. In this equation, t means the ages of testing.

$$CH^t_{\text{consumed by pozzolana}} = \overbrace{CH^t_{\text{control}} + \text{Carbonated } CH^t_{\text{control}}}^{\text{Total CH in control cement}} - \overbrace{(CH^t_{\text{blended}} + \text{Carbonated } CH^t_{\text{blended}})}^{\text{Total CH in blended cement}} \quad (1)$$

However, we assumed that:

- All CH produced in hydrating cement pastes reacted with CO_2 producing Cc (carbonation) and with SCM producing CSH (the pozzolanic reaction), or it remained as available CH in pastes. All of these were measured by TGA.
- The carbonation of CSH is negligible.

For analysis, in cases where the CH consumed by pozzolanic reaction was positive, this is the amount of CH which reacted with SCM because of the pozzolanic reaction. Otherwise, this suggests that SCM in blended cement pastes showed higher amount CH than that found in plain ones because of the induced effects on cement hydration like the filler effect, significant content of reactive silica, higher surface and the cation content of zeolites as reported by other authors (Antiohos & Tsimas, 2005; Kumar & Kumar, 2011; Lothenbach & Scrivener, 2011), or SCM mainly induced more carbonation in blended cement pastes than in plain ones (Sato & Beaudoin, 2007).

2.5.3. *Scanning electron microscopy*

For blended cement pastes, SEM-EDS measurements were done under Inspect® FEI SEM equipped with an EDS detector to analyse the chemical compositions. The operating conditions at low-vacuum mode were pressure at 30 Pa, 5 kV, 2 as spot size for imaging and 6 as spot size for analysing at EDS. These measurements were done at a magnification of 5000×.

2.5.4. *Density*

In order to evaluate the density of cement pastes, the procedure based on ASTM C20 *Standard Test Methods for Apparent Porosity, Water Absorption, Apparent Specific Gravity and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water* was

used. The analytical balance was a Metler Toledo® Excellence plus, which is a highly precise analytical balance and takes into account corrections due to temperature. As the samples were soaked in ethanol, the wet small pieces were dried in a desiccator for a while. Once they were dried, measurements were carried out in air condition. Then, the weighted dry sample was put into a beaker previously filled with distilled water and another measurement was done under water after waiting for the weight to stabilise.

3. Results and discussion

3.1. *Effect of SCMs on hydration products*

X-ray diffractograms of hydrating blended cement pastes over time show almost similar patterns as can be seen in Figure 1. We observed small differences in the peak heights of hydration products like CH over time, as well as the presence of "surviving" peaks of anhydrous cement phases at ages as late as 91 days. This suggests that a slow hydration process proceeded after 7 days.

Table 3 shows that Zeo2 was able to fix enough amount of CaO to be considered as pozzolana at ages as early as 7 days according to EN-196-5; in contrast, Zeo1 and Limo achieved this performance after 7 days. This could be due to the high cation exchange capacity of Zeo2, in part, composed of HEU–CLI and reportedly identified by other authors as the main Ca-consuming factor at least at early ages (Luke, 2007; Snellings et al., 2009).

Figure 2 presents the mineral compositions and the amorphous content in hydrating cement pastes calculated by Rietveld refinement method. Additionally, ettringite (AFt), iron-substituted ettringite (Fe-AFt) and tetracalcium hydrate (C_4AH_{13}) were only qualitatively identified by TGA-DSC analysis (Sha & Pereira, 2001a, 2001b). It is noteworthy that the main hydration products were identified as CH, CSH, AFt, kuzelite-monosulfate (AFm), C_4AH_{13}, Cc and scawtite (Sc) combining either techniques. In addition, C3S and C2S have both been found in the hydrating pastes, even at the age of 91 days. Another mineral phase, Qz, found in as-received zeolite tuffs, was also identified during the whole experimental time. This indicates that no chemical reaction involving Qz took place during hydration up to 91 days. Likewise, neither MOR nor HEU–CLI could be identified at such ages, thus revealing their complete reactions.

Figure 2 also suggests that the formation of CSH was accelerated at early age (assuming that it is the amorphous phase in QXRD (Matsushita & Hoshino, 2007)); in contrast, the CH production was delayed thereafter. In case of CSH, about 90% of total amount was already formed before 7 days. In case of CH, its content formed at early hydration remained almost unaltered over time. It seems that reactive silica played a crucial role in promoting the formation of CSH. But all SCMs showed almost the same amount of reactive silica (cf. Table 1).

Since lower W/B ratios produce a highly dense cementitious matrix in which the water inside pores is diminished, the pozzolanic reaction, at such a condition, could be a relatively slow process using non-evaporable water for reaction, as has been proposed by other authors (Brouwers, 2004, 2005; Igarashi & Kawamura, 2004; Loukili & Khelidj, 1999).

It is also observed in Figure 2 that the amounts of C3S and C2S were highly variable. These amounts sometimes even increased when they should normally deplete over time. Some authors have reported similar variations in XRD results before (Cuberos & De la Torre, 2009; Scrivener & Füllmann, 2004). The increase in the amount of anhydrous cement phases could be related to self-desiccation because of low

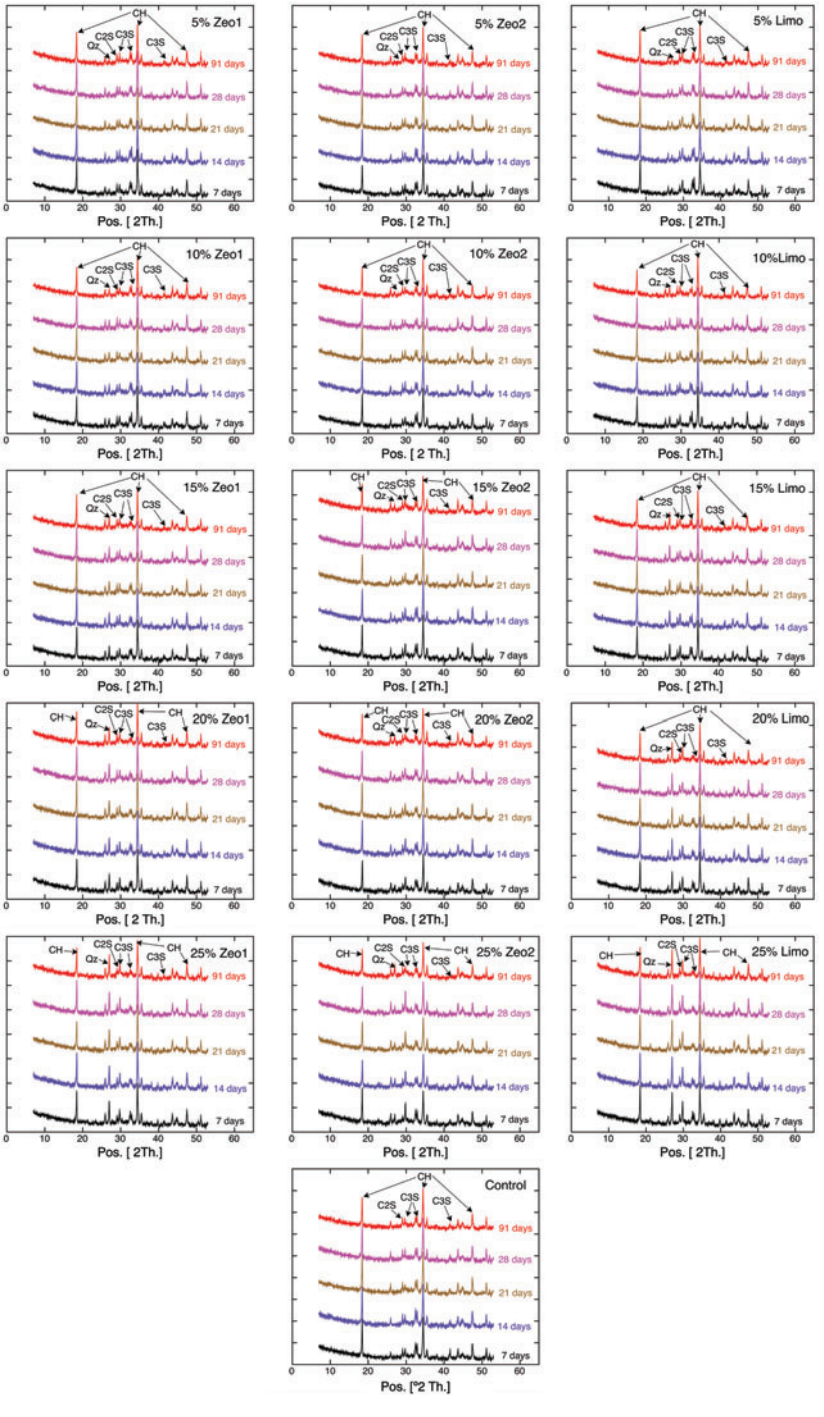

Figure 1. X-ray diffractograms of hydrating plain and blended cement pastes. CH: calcium hydroxide; C3S: tricalcium silicate; C2S: dicalcium silicate; non-assigned peaks belonging to corundum (internal standard in Rietveld refinement).

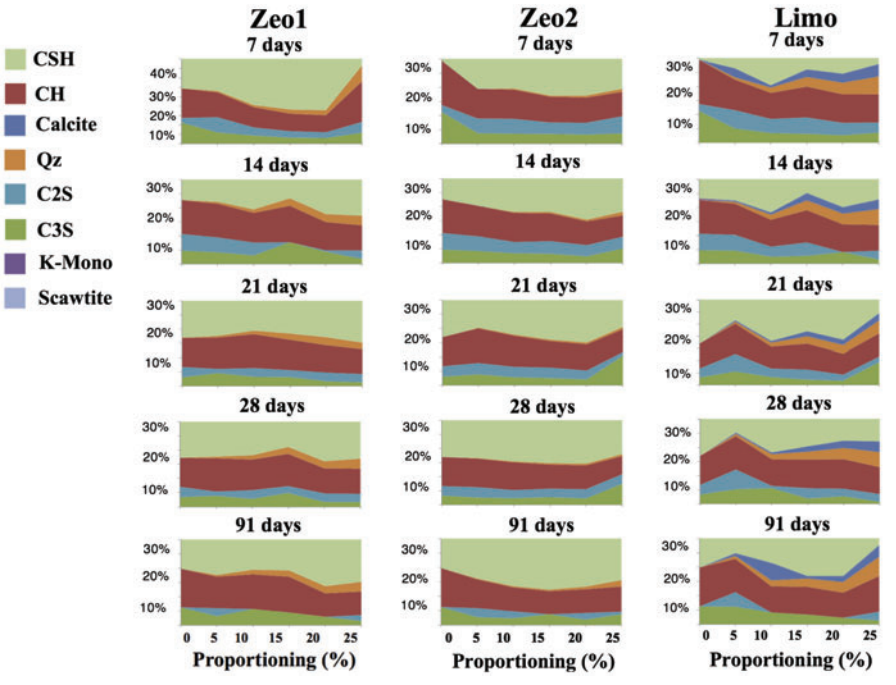

Figure 2. Comparison between plain and blended cement pastes at the same age in terms of amount of hydration products and unhydrated cement phases.

W/B ratio and significant replacement of pozzolana (Baghabra Al-Amoudi, Al-Kutti, Ahmadi, & Maslehuddin, 2009; Jensen & Hansen, 1999; Meeks & Carino, 1999).

On the other hand, Sc, a carbosilicate hydrate, was found in Limo-blended cement pastes because of the reaction of Cc with hydrating products (Kakali & Tsivilis, 2000).

Taking into account that the reduction of CH content could in part be attributed to the pozzolanic reaction and carbonation, a normalisation of these parameters to the cement content is also necessary to eliminate the dilution effect, which affects the CH content and the hydrates. Accordingly, in Figures 3 and 4, the content of CH and water in hydrates were normalised to cement content, respectively.

Once the dosage effect is diminished by normalisation, chemical reactions, i.e. the pozzolanic reaction and the carbonation, can only deplete the available CH content, thus allowing the evaluation of the proportion that induced these reactions. As expected, the overall trend of normalised content of CH (i.e. mg of CH per mg of cement in Figure 3), which was calculated by TGA, is higher in plain cement pastes than that in blended ones. It is noteworthy that similar patterns could be observed between calibration and replication, which were two slight different experimental settings. Hence, these similarities observed between these experimental settings allow to be confident in these results. It was also observed that SCM could accelerate CH production at early ages because of induced effects like the filler effect, reactive silica, higher surface and the cation content of zeolites; this effect continued up to 21 days, but later it remained almost constant. In the long term, almost all blends presented lower amount of CH than that of plain cement paste. However, there were two unexpected results, i.e. 15 and 25% Zeo1 blended at 91 days, which were higher than those of plain cement ones. These could be

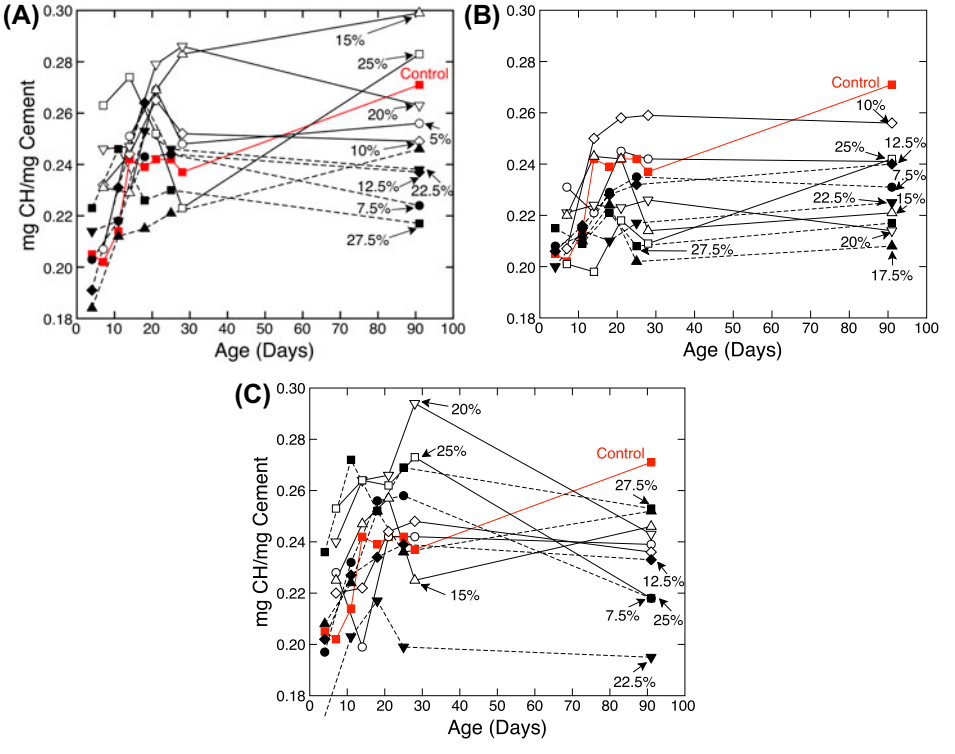

Figure 3. CH content normalised to cement content in blended cement pastes: solid line for calibration and dashed-line for replication. (A) Zeo1, (B) Zeo2 and (C) Limo.

interpreted as due to experimental error because it is not possible to produce more CH in blended cement pastes than in plain ones at such an age. Moreover, Figure 3 also shows some peaks in the range of 14–21 days that could be explained as accelerating the effect of pozzolana over alite (Escalante-Garcia & Sharp, 1998) and the start of belite hydration. Other authors have reported that the CH consumption, pozzolanic reaction and strength indexes were somehow increased in the range of 14–21 days (Loukili & Khelidj, 1999; Wild & Khatib, 1997). In summary, as the dosage increased, the amount of CH per mg of cement decreased; and Zeo2 was the most effective mineral addition to consume the CH available as was before seen in Frattini's test (cf. Table 3).

Figure 4 presents the evolution of normalised water involved in hydrates in cement pastes calculated by dividing a given weight of water with the whole weight of sample at a given age; afterwards, it was normalised to cement content and presented as a percentage. We can notice that the 'net' amount of water contained in hydrates of blended cement pastes was higher than that in plain cement pastes. Although there are many different hydrated phases containing different amounts of water, this is a good indicator that shows the net evolution of the hydration over time (Richardson, 2008). We can also notice small peaks that could be identified in the range of 14–21 days as was observed in other graphs. This could be explained as a higher amount of hydrates because of an increase in CH amount.

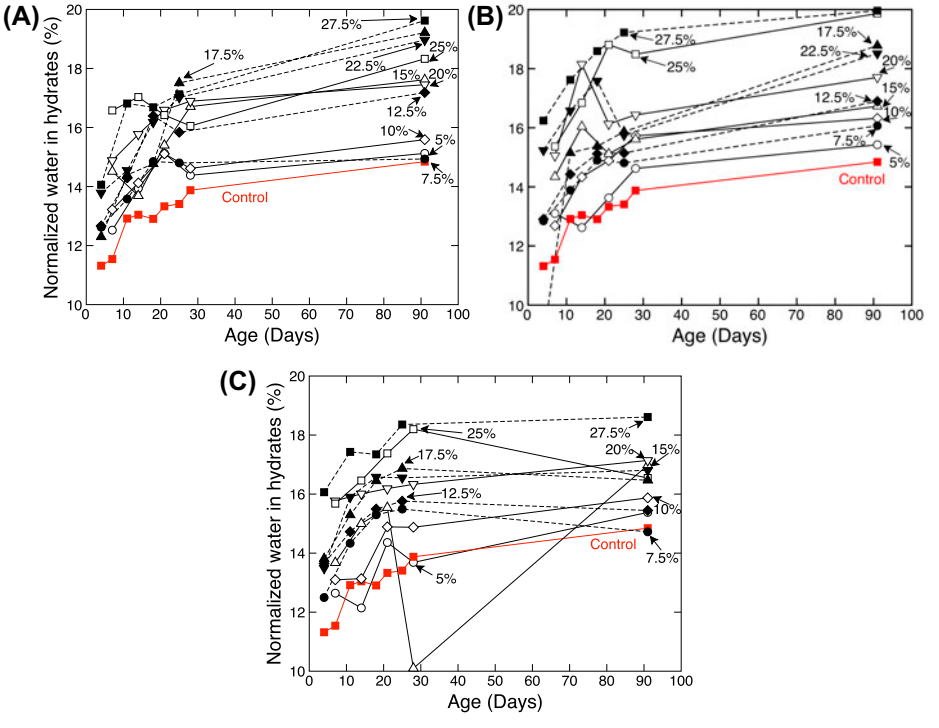

Figure 4. Percentage of normalised water in hydrates over time: solid line for calibration and dashed line for replication. (A) Zeo1, (B) Zeo2 and (C) Limo.

Generally, as dosage increased, the normalised water in hydrates also increased. In this sense, the relationship between dosage and normalised water in hydrates could be established by a linear equation. The best fit was achieved by using a linear equation up to 27.5% of replacement. The main parameters of the slope-intercept form of linear equation for blended cement pastes are summarised in Table 5. As a result, Zeo2-blended cement paste produced the highest content of hydrates under wet curing condition; however, it is noteworthy that the overall trend for all blended cement pastes was almost the same.

As has been reported before, fully hydrated cement paste should incorporate about .23 g of water per g of cement for plain cement paste; however, this value does not take into account the water-filled pore which is also available for reaction (Hover, 2011). Since a low W/B ratio was used, water-filled pore could be diminished because of its highly

Table 5. Slope-intercept form of the linear equation of normalised water and proportioning.

	Parameters		
SCM	$\frac{\Delta\%\text{ normalised water}}{\Delta\%\text{ proportioning}}$	b	R^2
Zeo1	.130	13.43	.954
Zeo2	.189	12.73	.894
Limo	.157	12.86	.882
Average	.158	13.00	.910

dense matrix. The amount of water incorporated into such a low W/B ratio cement pastes was of .14 g of water per g cement at the age of 91 days. This means that only 60% of the total amount of water used in fully hydrated cement pastes was partially incorporated in blended cement pastes. On the other hand, we also observed that if the percentage of SCM increased by 1%, then the normalised water in hydrates also increased by a factor of .158% under wet curing conditions, as can be seen in Equation (2).

$$\text{Normalised water in inhydrates } (\%) = .158 \times \text{dosage } (\%) + 13.00 \quad (2)$$

One possible explanation could be that these zeolitic tuffs acted as an internal water reservoir. In this case, both zeolitic tuffs showed 10% of mass loss up to 150 °C during thermal analysis (Cornejo et al., 2014); hence, it is possible that these tuffs could supply extra water for further hydration. However, zeolitic structures were not identified in X-ray diffractograms in the long term. Since the zeolite structure was dissolved during early hydration, this extra water could be consumed at early age, and it should not be available any more. In case of Limo, it also contained Qz, reactive silica, Cc and was less porous than zeolites, but it produced almost the same amount of hydrates as the zeolite tuffs did. This suggests that other chemical processes could affect the hydration. One of these could be the carbonation in pozzolana-blended cement pastes (Vigil de la Villa, Fernández, Rodríguez, García, & Villar-Cociña, 2013). In carbonation, apart from calcium carbonate production, water can be available as a product of the reaction between carbonic acid and C3S (Fernandez Bertos, Simons, Hills, & Carey, 2004). This extra water could, therefore, take part in further hydration, thus increasing the hydrates.

The amount of Cc in blended cement pastes, which was calculated by using TGA, for both the experimental settings, i.e. calibration and replication, is illustrated in Figure 5. These plots suggest that these zeolitic tuffs induce the carbonation process. In fact, as dosage increased, the content of Cc increased too. According to the figure, Limo showed the highest values of Cc in blended cement pastes. It is also observed that Zeo1 blends contained more Cc than Zeo2 ones, despite both showing almost the same chemical composition, reactive silica. This suggests that Zeo1 blends are more susceptible to carbonation than others. It is noteworthy that the results of Figure 5 can hardly be correlated to those of Figure 2 because two different methods, based on different physical interactions, were used, i.e. TGA and QXRD, respectively. Since XRD can be only quantified crystalline phases, amorphous phases were treated as whole amorphous content without any distinction. On the other hand, TGA can quantify the whole amount of Cc despite crystalline state; hence, the amount of Cc and lime calculated by TGA is generally higher than those calculated by XRD (Escalante-Garcia & Mendoza, 1999).

As a matter of fact the carbonation depends, among others, on W/B ratio. Khan et al. concluded that as the dosage increased, so did the carbonation using a W/B ratio of .27 (Khan & Lynsdale, 2002). Bilim has conversely reported that zeolites improved the durability of carbonation using a W/B ratio of .5 (Bilim, 2011). This suggests that the W/B ratio, which promotes the pozzolanic reaction instead of carbonation, is higher than .42; conversely, at lower ratio, carbonation is promoted instead of pozzolanic reaction (Reference in Meeks & Carino, 1999). In other words, if CH is vigorously consumed by the pozzolanic reaction, its depletion will reduce the likelihood of it being carbonated (Jiang, Lin, & Cai, 2000). Keeping in mind these results, as a W/B ratio of .3 was used, the studied blended cement pastes showed such lower resistances against carbonation.

The plot of the density of pozzolana-blended cement pastes as a function of time can be seen in Figure 6. The overall result presents that the density of control sample is

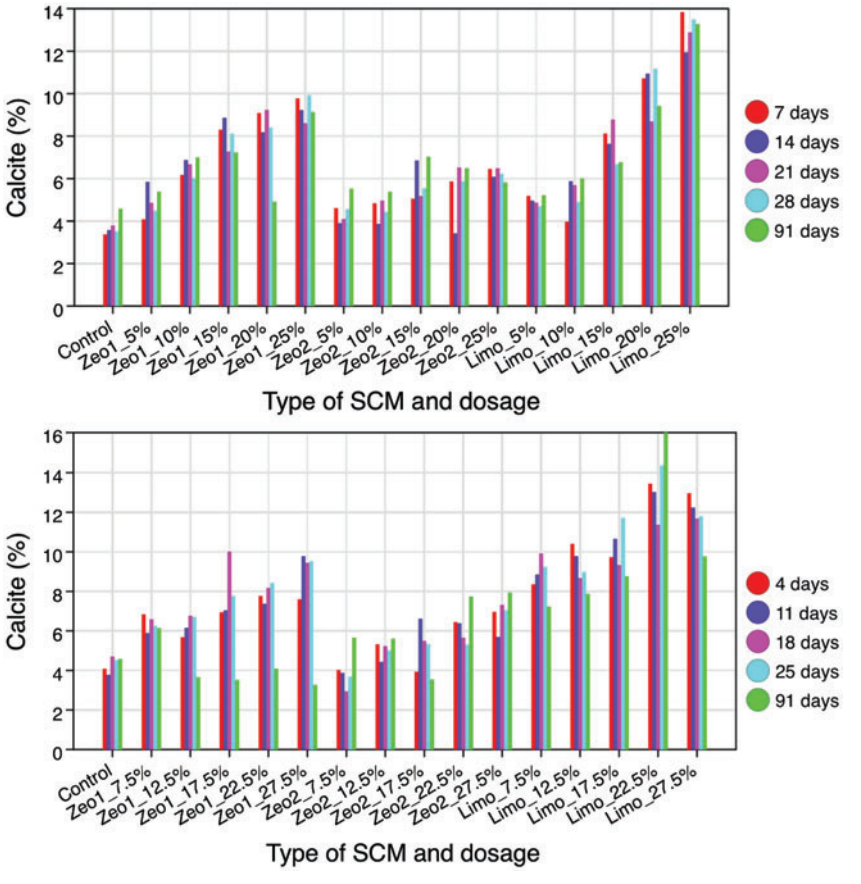

Figure 5. Content of calcium carbonate in plain and blended cement pastes: calibration on the top and replication on the bottom.

higher than that of SCM-blended cement pastes. It is due to the usage of meaningful amounts of mineral additions, which are lighter than anhydrous cement grains, thus leading to the decrease of density as dosage increases. At the same time, an increase in density over time was also observed and attributed to the formation of hydration products inside the pore system. Accordingly, as hydration product increased, so did the density. In this case, Zeo2-blended cement paste showed the lowest density; in contrast, Zeo1 and Limo displayed almost the same values.

In addition, there is an unexpectedly high value of density at the age of 11 days within control results. It is noteworthy that although other hydration parameters showed a meaningful variation in results at ages from 14–28 days, none of them could explain this outstanding value of density at this age. Therefore, this unexpected value could be related to the uncertainty in the weighting procedure within two different media, i.e. under water and in air.

We also observed that as the content of Cc increased, so did the density. It seems that this behaviour could be due to the fact that Cc is heavier than other hydration

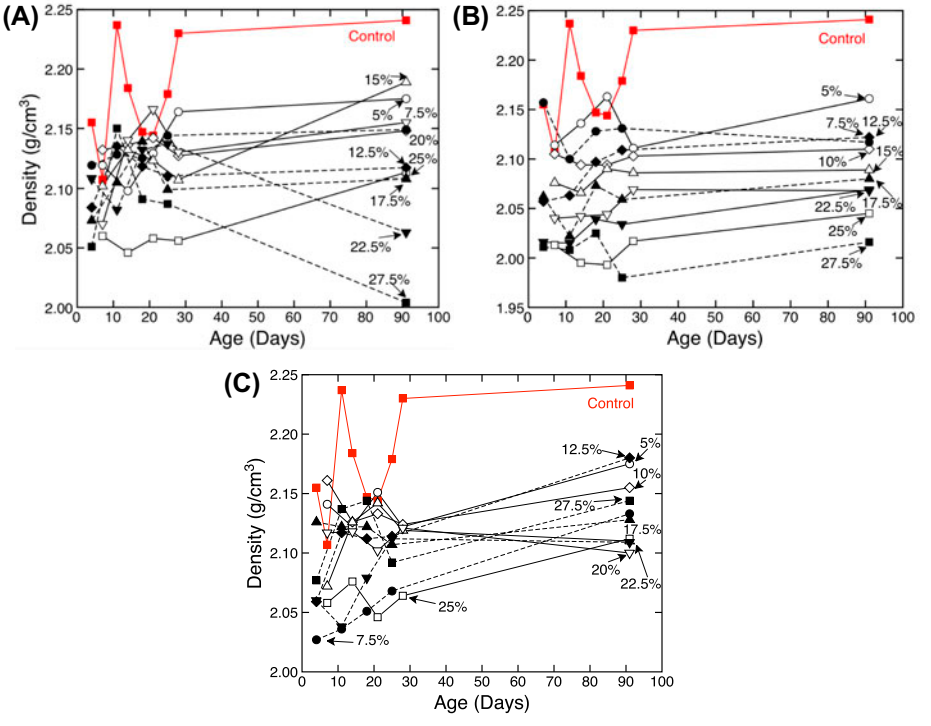

Figure 6. Density of pozzolana-blended cement pastes: solid line for calibration and dashed line for replication. (A) Zeo1, (B) Zeo2 and (C) Limo.

products, including CSH and CH (Balonis & Glasser, 2009); hence, an increase in Cc in the cement paste could lead to increase in density (Borges et al., 2010).

As mentioned before, dilution and carbonation should be taken into account in order to evaluate the pozzolanic reaction because of their effects over the CH content during the hydration. Figure 7 summarises the results of the amount of CH which reacted with pozzolana in accordance with Equation (1). According to this, the pozzolanic reaction started at the age of 25 days and proceeded beyond the age of 91 days. The amount of CH consumed by the pozzolanic reaction presented a maximum value of .1 mg CH consumed by the pozzolanic reaction per mg cement at an age of 91 days. In this sense, the average percentage of CH consumed by pozzolana could be 8% of the total amount of CH formed during the hydration up to 91 days.

The plots of the consumption of CH by the pozzolanic reaction, given in Figure 7, also indicate that the pozzolanic reaction consumed the CH at different rates. In case of Zeo2, it was better in consuming the CH than the others; however, some blends of Zeo1 and Limo also showed such consumptions at the age of 91 days. As expected, Limo was the worst in consuming the CH. In this figure, small peaks are also observed in the range of 14–21 days attributed to the onset of belite hydration. These graphs also show that the lower the dosage, the higher the amount of CH consumed by pozzolanic reaction, although this effect diminished as time progressed.

Although the Cc identified in raw materials, i.e. Zeo2 and Limo, was removed from calculation, we observed that the average percentage of total carbonated CH was 19%

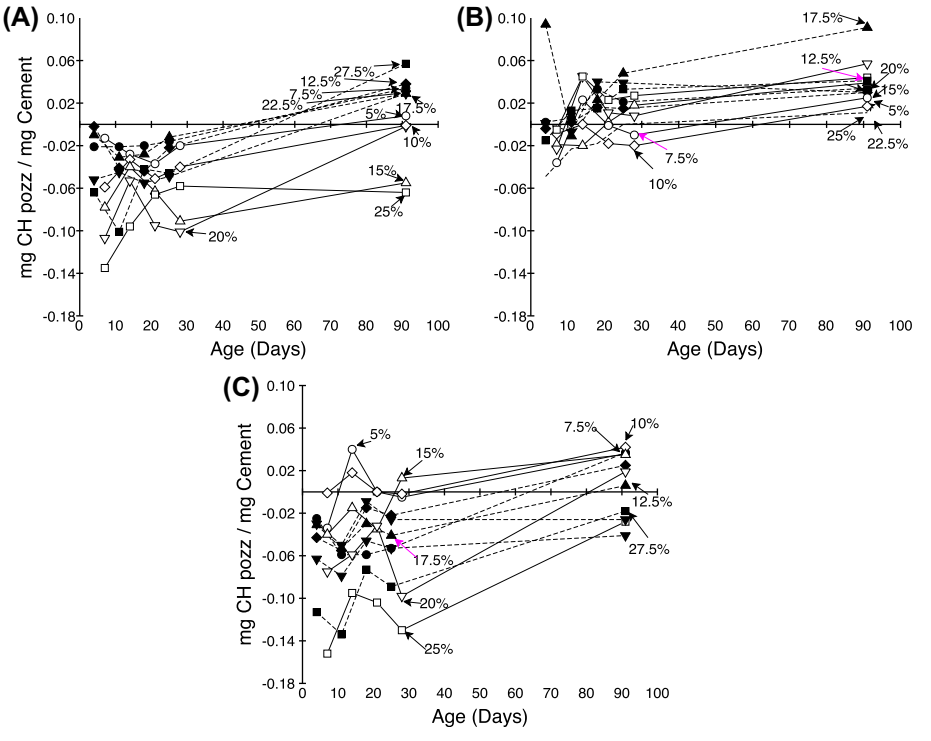

Figure 7. Evolution of the amount of CH consumed by the pozzolanic reaction (difference between total CH content in blended and control cement pastes) over the amount of cement for calibration (solid line) and for replication (dashed line). (A) Zeo1, (B) Zeo2 and (C) Limo.

of the total amount of CH produced during the hydration up to 91 days. Hence, the amount of CH transformed by carbonation was almost twice as higher than that by the pozzolanic reaction under this experimental condition.

3.2. *Effects of SCMs on compressive strength and microstructure*

Because of engineering applications, it is important to find out which dosage performed the best in terms of compressive strength. Hence, a comparison between Zeo1-, Zeo2- and Limo-blended cement pastes in terms of compressive strength is shown in Table 6. In this table, proportioning is proved to exert a meaningful effect on compressive strength in the long term. We can also notice that most of the blended cement pastes showed a slow strength-gaining rate at early ages up to 14 day despite the presence of significant amounts of reactive silica. On the other hand, in the range of 14–91 days, the blends developed the highest values. In case of Zeo1-blended cement pastes, these showed higher compressive strength than control after 21 days. In case of Zeo2-blended cement pastes, some of them showed higher than control at an age of 91 days. And in case of Limo-blended cement pastes, only three dosages could show higher than control at an age of 91 days.

As a result, Zeo1-blended cement pastes performed better than the others, followed by Zeo2-blends and finally Limo-blended cement pastes. It is noteworthy that the best

Table 6. Least squares means with standard errors of compressive strength (MPa) for each level of dosage (%) and ages of testing (days).

	Zeo1		Zeo2		Limo	
	Mean	St. error	Mean	St. error	Mean	St. error
Calibration						
Control	95.04					
Grand mean	94.25		93.77		86.46	
Proportioning (%)						
5	97.32	3.49	101.29	2.95	89.77	3.44
10	99.02		89.61		93.75	
15	103.56		92.49		86.84	
20	88.63		98.82		83.88	
25	81.92		85.39		69.45	
Age of testing (days)						
7	74.30	3.18	82.17	2.69	65.84	3.14
14	85.12		93.06		82.51	
21	91.90		96.86		88.08	
28	106.72		91.17		94.44	
91	113.21		105.59		101.42	
Replication						
Control	95.84					
Grand mean	89.36		86.30		78.55	
Proportioning (%)						
7.5	92.27	3.48	88.44	4.33	71.89	3.30
12.5	95.02		82.48		85.96	
17.5	83.92		86.73		82.26	
22.5	91.19		85.59		63.77	
27.5	77.93		78.75		71.56	
Age of testing (days)						
4	65.95	3.17	56.85	3.95	53.17	3.01
11	86.65		87.95		74.50	
18	89.26		91.83		86.48	
25	98.99		88.37		84.60	
91	105.95		106.50		93.98	

ranges of dosages were: in Zeo1-blends, from 12.5 to 15%; in Zeo2, from 17.5 to 20%; and in Limo, from 10 to 12.5%.

We also noticed that long-term performance of blended cement pastes depended strongly on hydration process at early age. This suggests that mineral addition induces an accelerating effect over hydration product and microstructure improving in compressive strength, but inducing carbonation.

Those high values of the compressive strength were in part related to CH consumed by pozzolana indicating that the pozzolanic reaction positively contributes to the improvement of compressive strength. However, most CH-consuming zeolite-blended cement pastes did not show the highest compressive strength. It suggests that other factors like microstructure and carbonation also played remarkable roles in affecting the compressive strength.

In order for the microstructure to analyse, a comparison between plain and blended cement pastes at 7 and 91 days is shown in Figure 8. It is noteworthy that the difference between plain and blended cement pastes was mainly attributed to well-crystallized CH

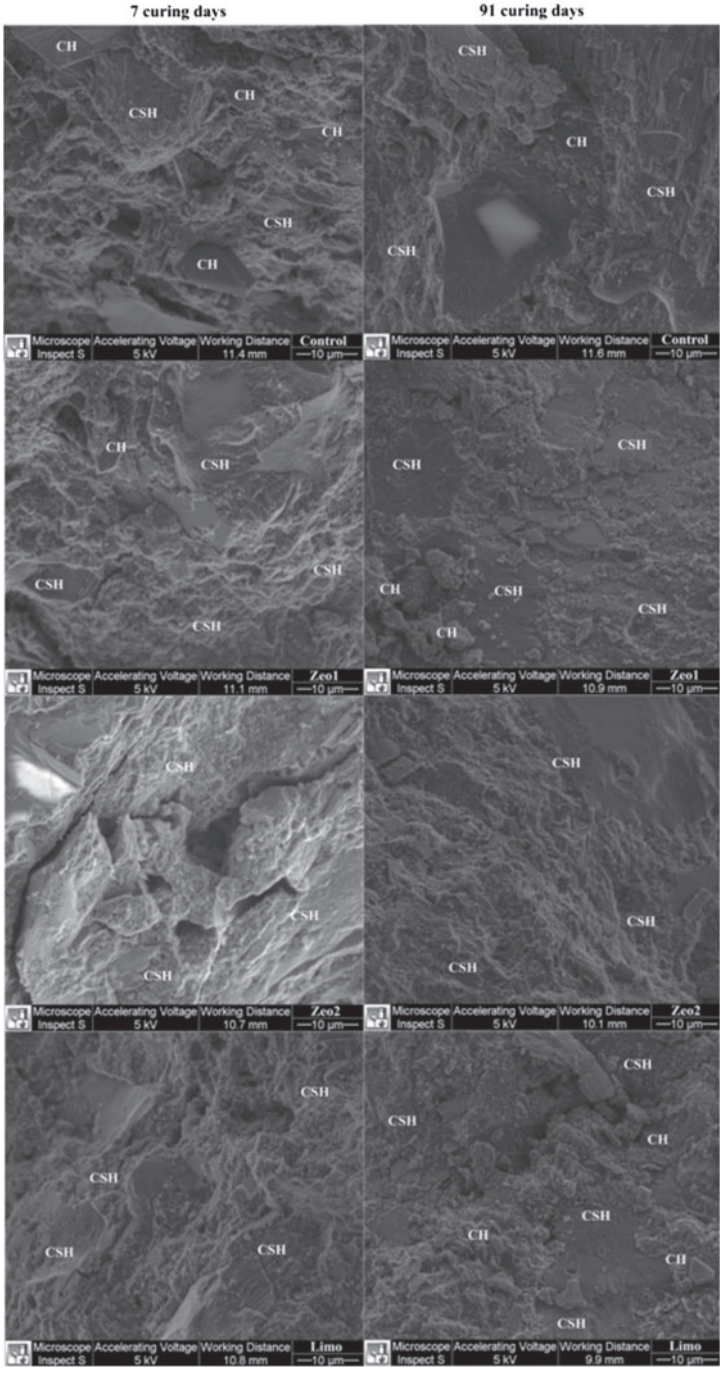

Figure 8. Comparison of fractured specimens between 7 and 91 days for plain and Zeo1, Zeo2 and Limo cement pastes using 25% of replacement. In these images, CH and CSH have been highlighted, but only in plain cement pastes; CH can be seen as well-defined crystal.

easily found in plain cement pastes. Apart from this, similar massive structure found at both ages.

4. Conclusion

After analysing the SCMs, i.e. Zeo1, Zeo2 and Limo, under wet curing condition at W/B ratio of .3, varying dosages and curing times, the following conclusions can be drawn:

(1) The development of hydrating phases identified by XRD showed various production rates. In case of CSH, around 90% was already produced at the age of 7 days, and in case of CH, its content remained almost unaltered thereafter.
(2) In all blended cement pastes, normalised CH content decreased as proportioning increased. This behaviour was mainly influenced by the pozzolanic reaction as well as carbonation.
(3) The carbonation increased as the dosage increased. These natural zeolites and Limo-blended cement pastes were susceptible to carbonation. Among the zeolites, MOR-rich tuff proved to be more susceptible to carbonation than HEU–CLI tuff. Regardless of the fact that these zeolites had almost the same chemical composition, their differences in terms of crystalline state and microstructure probably affected their susceptibility to carbonation.
(4) Blended-cement pastes produced higher amount of hydrates than plain cement pastes. As dosage increased, so did the amount of hydrates. The main hydrate phases produced during hydration were CH and CSH.
(5) The result of normalised water in hydrates at 0% of replacement was .14 g of water per g cement at the age of 91 days under wet curing conditions. It suggests that only 60% of the total amount of water used in fully hydrated cement pastes was partially used at such a low W/B ratio despite wet curing conditions. However, this value was significantly affected by the dosage. An increase in dosage can lead to increase in water in hydrates. The percentage of pozzolana increased by 1% on average and the normalised water in hydrates was also increased by a factor of .158% under these experimental conditions.
(6) The total amount of CH consumed by pozzolanic reaction was likely to be around 8%, while carbonation transformed around 19% of the total amount of CH at 91 days.
(7) Zeo1-blended cement pastes showed the highest compressive strength and contained the highest amount of carbonated CH, but they did not show the highest amount of CH consumed by the pozzolanic reaction.
(8) The microstructure was influenced by mineral addition and curing condition at early ages. No meaningful difference in the microstructure at 91 days was observed.

In this study, the relationship between consumption of CH and pozzolanic reaction has been established; carbonation and dilution, as well as their effect on compressive strength and microstructure has been successfully carried out and the results are in accordance with scientific literature.

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